

## Synthesis and Crystal Structure of the Volatile Monocyclopentadienyl Uranium Complex $(\eta\text{-C}_5\text{H}_5)\text{U}(\text{BH}_4)_3$

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Treatment of  $\text{U}(\text{BH}_4)_4$  with  $\text{Ti}(\eta\text{-C}_5\text{H}_5)$  or cyclopentadiene in toluene affords the title compound, the structure of which has been determined.

The structural properties of the covalent uranium tetra-borohydride  $\text{U}(\text{BH}_4)_4$  (1) has received much attention,<sup>1</sup> in particular because of its volatility.<sup>2</sup> However, the chemical transformations of (1) are limited to the synthesis of alkyl-triborohydride derivatives<sup>3</sup> and the preparation of ether and phosphine adducts of (1) or  $\text{U}(\text{BH}_4)_3$ .<sup>4</sup> It seemed to us that it would be interesting to prepare organouranium complexes by substitution of the  $\text{BH}_4^-$  groups of (1) with hydrocarbon ligands. Such a reaction led to the volatile compound  $(\eta\text{-C}_5\text{H}_5)\text{U}(\text{BH}_4)_3$  (2) which is a rare example of a monocyclopentadienyl uranium complex.<sup>5</sup> Here we describe the synthesis and the *X*-ray crystal structure of (2).



The reaction of (1) in tetrahydrofuran (THF) with 2 or 3 equiv. of  $\text{Ti}(\text{cp})$  ( $\text{cp} = \eta\text{-C}_5\text{H}_5$ ) gave respectively the cyclopentadienyl products  $(\text{cp})_2\text{U}(\text{BH}_4)_2$ <sup>6</sup> (3) and  $(\text{cp})_3\text{U}(\text{BH}_4)$ <sup>7</sup> (4); (4) reacted with  $\text{Bu}^n\text{Li}$  to give the alkyl complex  $(\text{cp})_3\text{UBu}^n$ .<sup>8</sup> When treated with 1 equiv. of  $\text{Ti}(\text{cp})$ , (1) was half-transformed into (3); the desired product (2) could not be obtained in THF.

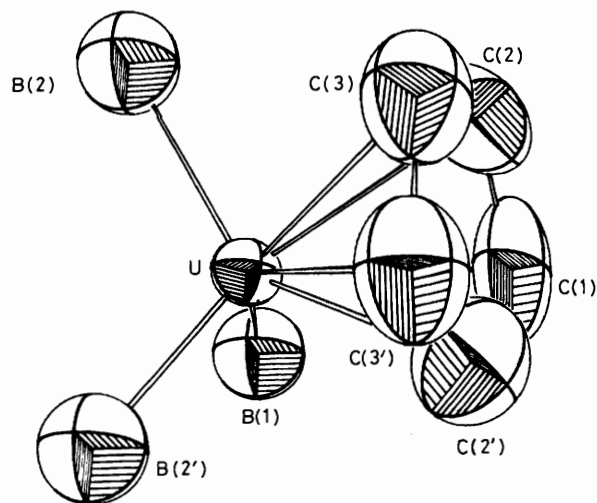
The monocyclopentadienyl compound (2) was prepared in 55% yield from the reaction of (1) (163 mg) with  $\text{Ti}(\text{cp})$  (140 mg) in toluene or pentane (40 ml); the mixture was stirred at 20 °C for 18 h, filtered, and evaporated *in vacuo* below 20 °C. Compound (2) was alternatively obtained in 60% yield by the reaction of (1) (90 mg) with cyclopentadiene (0.4 ml) in toluene (10 ml) at 80 °C for 3 h. Sometimes, traces of (3) were formed during these reactions. That co-ordinating solvents must be avoided in the syntheses of (2) was further illustrated by the total conversion of this complex, in the presence of

THF, into a 1:1 mixture of (3) and the THF adduct of (1),<sup>4b</sup> whereas in toluene, the equimolecular mixture of (3) and (1) was completely transformed into (2). Whatever its mode of preparation, (2) was extracted with pentane, purified by sublimation ( $10^{-2}$  mmHg, 20 °C) and isolated as orange crystals.†

The structure‡ (Figure 1) consists of discrete molecules of  $(\eta\text{-C}_5\text{H}_5)\text{U}(\text{BH}_4)_3$ . The cyclopentadienyl and borohydride

† Complex (2) gave satisfactory elemental analyses (C,H,B,U). Selected spectroscopic data:  $\delta(^1\text{H}, 60 \text{ MHz}, \text{C}_6\text{D}_6)$  53.20 (12 H, q,  $J_{\text{BH}}$  78 Hz,  $\text{BH}_4$ ) and 14.63 (5H, s, cp);  $\nu(\text{mull})$  2528, 2156, 2087, and 1208  $\text{cm}^{-1}$  (tridentate<sup>1</sup>  $\text{BH}_4$ ); 3100, 1015, and 806  $\text{cm}^{-1}$  ( $\eta\text{-C}_5\text{H}_5$ ).

‡ *Crystal data* for (2):  $\text{C}_5\text{H}_7\text{B}_3\text{U}$ , orthorhombic, space group *Cmc*2<sub>1</sub>,  $a = 11.130(4)$ ,  $b = 13.220(7)$ ,  $c = 7.550(2)$  Å,  $U = 1110$  Å<sup>3</sup>,  $Z = 4$ ,  $D_c = 2.08$  g  $\text{cm}^{-3}$ ,  $\mu = 137.92$   $\text{cm}^{-1}$ . The experimental data were collected with a CAD-4 diffractometer (Mo- $K_\alpha$  radiation) in the range  $4^\circ < 2\theta < 50^\circ$ . 453 Reflections with  $I > 3\sigma(I)$  were used after Lorentz, polarization, and empirical absorption<sup>9</sup> corrections. The structure was solved by analysis of the Patterson function and successive Fourier syntheses. Hydrogen atoms of the cp ring were introduced in idealized positions and constrained to ride on their parent carbon atoms. Hydrogen atoms of the  $\text{BH}_4^-$  groups were not located. Analytical scattering factors for neutral atoms were corrected for  $f'$  and  $f''$ . U and C atoms were refined anisotropically. The centric uranium atom position dominated the structure factors leading to some ambiguity in space group choice and to less accurate positions of the light atoms. The non-centrosymmetric structure converged with  $R_f = 0.0325$  and  $R_w = 0.0360$ . The final difference map showed no peaks exceeding 0.5 e Å<sup>-3</sup> (except +0.9 and 0.7 near the U atom). The atomic co-ordinates are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.



**Figure 1.** The X-ray crystal structure of (2). Some important distances and angles: U–C(1) 2.60(3), U–C(2) 2.65(3), U–C(3) 2.72(3), U–B(1) 2.57(5), U–B(2) 2.46(4), C(1)–C(2) 1.33(5), C(2)–C(3) 1.27(5), C(3)–C(3') 1.34(5) Å;  $\angle$  centroid cp–U–B(1) 120(2), centroid cp–U–B(2) 111(2), B(1)–U–B(2) 100(2)°. The distance between the U atom and the cyclopentadienyl ligand plane is 2.42(3) Å.

ligands form a distorted tetrahedron around the uranium atom. The short U–B distances are characteristic of tridentate  $\text{BH}_4^-$  ligands.<sup>1</sup> The plane of the boron atoms and that of the cyclopentadienyl ligand are parallel and orthogonal to the plane of symmetry of the molecule defined by the U, C(1), and B(1) atoms.

The remarkable solubility in non-polar solvents and the volatility of (2) can be accounted for by the covalent and monomeric structure of this compound; to our knowledge, (2) is the only organouranium complex which exhibits a vapour pressure§ of the same order of magnitude as (1).

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### References

- 1 T. J. Marks and J. R. Kolb, *Chem. Rev.*, 1977, **77**, 263, and references cited.
- 2 H. I. Schlesinger and H. C. Brown, *J. Am. Chem. Soc.*, 1953, **75**, 219.
- 3 H. I. Schlesinger, H. C. Brown, L. Horvitz, A. C. Bond, L. D. Tuck, and A. O. Walker, *J. Am. Chem. Soc.*, 1953, **75**, 222.
- 4 (a) J. Brennan, R. Shinomoto, A. Zalkin, and N. Edelstein, *Inorg. Chem.*, 1984, **23**, 4143, and references cited; (b) R. R. Rietz, N. M. Edelstein, H. W. Ruben, D. H. Templeton, and A. Zalkin, *ibid.*, 1978, **17**, 658.
- 5 R. D. Ernst, W. J. Kenelly, C. S. Day, V. W. Day, and T. J. Marks, *J. Am. Chem. Soc.*, 1979, **101**, 2656; K. W. Bagnall, F. Benetollo, G. Bombieri, and G. de Paoli, *J. Chem. Soc., Dalton Trans.*, 1984, 67.
- 6 P. Zanella, G. de Paoli, G. Bombieri, G. Zanotti, and R. Rossi, *J. Organomet. Chem.*, 1977, **142**, C21.
- 7 M. L. Anderson and L. R. Crisler, *J. Organomet. Chem.*, 1969, **17**, 345.
- 8 T. J. Marks, A. M. Seyam, and J. R. Kolb, *J. Am. Chem. Soc.*, 1973, **95**, 5529.
- 9 N. Walker and D. Stuart, *Acta Crystallogr., Sect. A*, 1983, **39**, 158.

§ The vapour pressures (mmHg) of (1) and (2) at 25 °C were found to be 0.09 (0.10 in ref. 2) and 0.07 respectively.